Collecting and Preparing Soil Samples for VOC Analysis

Implementation Memorandum #5

To:	Interested Parties
From:	Tim Nord, Section Manager
Date:	June 22, 2004
Re:	Collecting and Preparing Soil Samples for VOC Analysis

Intent of this Memorandum

The purpose of this technical memorandum is to set forth guidance regarding the implementation of Method 5035A[1]. This technical memorandum provides detailed guidance on:

- How to collect soil volatile organic compound (VOC) samples;
- How to prepare and preserve soil VOC samples; and
- How to store soil VOC samples.

This guidance contains information on four methods that you may use to collect and prepare soil VOC samples for analysis. If you are collecting soil VOC samples, then you will need to use one or any combination of these four methods:

1. On-site laboratory,
2. Lab preservation,
3. Field preservation, and
4. Alternative methods.

[1] Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples, EPA SW-846.

Details on each of these four methods are provided in the body of this tech memo.

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What is Method 5035A?

EPA Method 5035A sets forth the requirements and procedures applicable to the collection and preparation of soil samples for volatile organic compound (VOC) analysis, including:

- Recommended or required sampling equipment (e.g., 40-mL volatile organic compound analysis (VOA) vials, etc.);
- How to collect undisturbed soil samples;
- How to preserve samples in the field by chemical (e.g., methanol) or physical (e.g., freezing) methods;
- How to transport and store samples; and
- Analytical options (i.e., low-level vs. high-level method).

Method 5035A was developed and approved for use in July 2002 by the U.S. Environmental Protection Agency (EPA). The method was included by EPA as a new method under SW-846, "Test Method for Evaluating Solid Wastes: Physical/Chemical Methods" (3rd Ed.).

When Should I Use Method 5035A?

WAC 173-340-830(3) specifies acceptable analytical methods for sites where a remedial action[2] is being conducted under the Model Toxics Control Act (MTCA) regulation[3]. EPA Method 5035A, which sets forth the requirements and procedures for the collection and preparation of soil samples for VOC analysis, is one of those methods.

Therefore, you must comply with the requirements of Method 5035A if:

- You are conducting remedial action under the MTCA cleanup regulation; and

[2] A "remedial action" includes remedial investigation /feasibility study (RI/FS) or site characterization (WAC 173-340-350).
[3] Chapter 173-340 WAC

- As part of that remedial action, you are collecting soil samples for VOC analysis.

Who is the Intended Audience for this Guidance?

The intended users of this guidance are those individuals involved in the collection and preparation of soil samples for VOC analysis, including:

- Site managers;
- Field sampling personnel;
- Laboratory analysts;
- Quality assurance personnel; and
- Data quality assessors.

The target audience for this guidance is anyone conducting petroleum- or chlorinated hydrocarbon investigations or cleanups. For example, you must use this sampling protocol for volatile hazardous substances such as benzene or trichloroethylene (TCE).

Why Do Soil VOC Samples Need to be Preserved?

A significant body of scientific evidence has found that VOCs will volatilize and biodegrade during sample collection and transport, which typically results in significant losses of initial VOC concentrations. Consequently, the consensus opinion of EPA and the scientific community is that you must take significant precautions when collecting and preparing soil samples for VOC analysis, including the use of preservation techniques, to limit the impacts of volatilization and biodegradation. Both of these mechanisms are discussed in more detail below.

Volatilization[4]

With respect to volatilization, when VOCs are released to the soil, they immediately start to partition from the liquid phase to the gaseous phase. This rate of volatilization is compound specific. Various soil properties also impact this rate of volatilization, including grain size, moisture content, and porosity. VOCs within disaggregated or disturbed soil samples also tend to volatilize at faster rates.

In most solid materials, the molecular diffusion coefficients of VOCs in the gaseous phase are high enough to allow for the immediate volatilization of those VOCs from a freshly exposed sample surface, resulting in a loss to the surrounding atmosphere. If the sample matrix is porous, these losses will continue as VOCs below the surface diffuse outward.

In summary, the primary goal of VOC sample collection and preservation techniques is to minimize or eliminate the loss of the compounds of concern through direct volatilization to the atmosphere.

Biodegradation[5]

The biodegradation of VOCs involves compound loss by biological processes mediated by naturally-occurring organisms found within the sample. Aerobic processes

[4] See Refs 1, 7, 9, 11, 18, 0, 27.
[5] See Refs 8, 10, 13, 16, 17, 24.

are of greatest concern, but anaerobic organisms can also result in significant compound loss. The rate of biodegradation is dependent upon several factors, including indigenous microbes, the chemical properties of the soil VOC, the original VOC concentration, and temperature.

Most soil sample collection procedures involve intrusive sampling operations that can create or enhance aerobic conditions within a sample. Aerobic conditions can occur by disaggregation of the soil particles or by simple exposure to the air. Once collected, soil VOC samples must be preserved or immediately placed in a sealed container. This must be done to minimize VOC losses from uncontrolled aerobic processes. If you do not take these precautions, then aerobic conditions will persist during handling and storage.

What is the Definition of VOC?

VOCs[6] are organic chemicals that easily vaporize at room temperature. This includes low molecular weight aromatics, hydrocarbons, halogenated hydrocarbons, ketones, acetates, nitriles, acrylates, ethers and sulfides. Most VOCs typically have boiling points in the range of 150-200° C.

[6] See also WAC 173-340-200 definition of VOC and EPA VOC definition in Method 5035A, Appendix A, Section A.1.1.

Should I Use this Sampling Method for Semi-volatiles?

No, you do not have to use this sampling method for semi volatiles (e.g., benzo(a)pyrene). The EPA Method 8270C is used for analyzing semi-volatiles.

Development of EPA Method 5035A

EPA Method 5035 was first published in Update III of the third edition of SW-846 on June 13, 1997. Since that time, the scientific community has continued to conduct research on soil sampling methods that minimize VOC losses. In this same time period (1997-03), EPA has also continued to provide information on issues related to Method 5035A.

On August 7, 1998, EPA published a clarification memorandum[7] on the use of SW-846 methods, including Method 5035. In the Aug-98 memorandum, EPA recommended the following:

- As a matter of policy, all soil VOC samples should be preserved in some manner, whenever possible.
- Do not use sodium bisulfate as a preservative in calcareous soil. Use the EnCore® Sampler instead.
- If methanol is used as a preservative, then check for losses by re-weighing, in the field, sample vials that were previously weighed in the laboratory.

[7] See Ref 6.

If the difference between the laboratory/field weight is > 0.2 g, then methanol loss may have occurred and the vial should not be used.

- Use a soil-to-solvent ratio of 1:1, e.g., 5 g soil and 5 mL of methanol.

In July 2002, EPA published an update to Method 5035 in the fourth update of SW-846. The updated method is now known as Method "5035A". The updated (Jul-02) Method 5035A now contains an appendix with 32 pages of additional information.

For further information regarding the requirements of Method 5035A as well as the basis for those requirements, please refer to the method, which is available electronically (EPA 5035A).

Which Soil VOC Sampling Method Should I Select?

You will need to use one or any combination of the following four methods: 1) on-site laboratory, 2) lab preservation, 3) field preservation or 4) alternative methods. **Detailed instructions on how to collect and preserve soil VOC samples using methanol or sodium bisulfate are provided in Appendix A: Soil VOC Sampling Instructions (p. 14).** Advantages and limitations of each of these four methods are discussed below.

Option 1: Mobile or On-site Labs

- The key advantage of this option is that you ***don't need to preserve*** any samples. You also get quantitative information in real time, which is extremely helpful for site characterizations. The one possible disadvantage of this option is cost.

Option 2: Lab Preservation

- If you opt for lab preservation, then you will collect ***unpreserved*** soil VOC samples, place them on ice @ 4 ± 2° C and ship them to the lab for preservation and analysis. Under Method 5035A, you will ship all unpreserved samples to the lab and the lab will receive and extract the samples ***within 48 hours of sample collection.*** Some sampling devices (e.g., **En Core® Sampler)** require you to submit samples to the lab within 48 hours.

- **Sample containers.** You may use some type of zero headspace extraction (ZHE) container (e.g., **En Core® Sampler**) or an empty 40-mL VOA vial with 0.25 mm thick PTFE-lined septa. *Do not use core barrel liners or sample cores wrapped in aluminum foil - this will not prevent volatilization!*

- **Preservation methods.** Once the samples arrive at the lab, they must either be ***preserved*** or ***analyzed*** within 48 hours from the time of sample collection. The chemical preservation method that is used will depend on the type of analysis, i.e., low- (sodium bisulfate) or high- (methanol) concentration method. Samples that are chemically preserved in the lab must then be

analyzed within required holding times (normally 14 days). You may also, as an option, utilize a physical preservation method by having the lab **freeze**[8] **non-preserved** soil VOC samples to **< -7° C** for up to **14 days**.

Note: If you do have the lab freeze samples, then the samples must be extracted with methanol only. You cannot freeze samples for the low-concentration (sodium bisulfate) method.

Advantages of Lab Preservation

- You do not need to bring preservative chemicals to the field. Also, you do not need to weigh samples prior to and after collection. Lastly, if you opt for preservation by freezing, it's convenient for the lab because the sample can be stored in a cooler for the 14-day holding time.

Limitations on Lab Preservation

- The one limitation of lab preservation is you must ship samples to the lab within ***48 hours from the time of sample collection!*** This does not mean, however, that the sample must be analyzed within 48 hours. What it does mean is that you must ship samples to the lab within 48 hours. The lab must then preserve the sample with sodium bisulfate, methanol, or by freezing to < -7° C. If this is done within 48 hours, the holding time is 14 days.

Option 3: Field Preservation

- If you opt for field preservation, then you will collect soil VOC samples and preserve in the field by chemical preservation methods using sodium bisulfate or methanol, or by a physical preservation method such as freezing.

- **Sample containers.** If you opt for chemical field preservation, then you will be using 40-mL VOA vials with PTFE-lined septa. The vials may be pre-preserved and pre-weighed in the lab, or, you can do this in the field.

- **Preservation methods.** The chemical preservation method that you use will depend on whether you use the low- or high-concentration method. If you plan to use the low-concentration method, you must add 5 mL of sodium bisulfate to a 5 g soil sample. If you use the high-concentration method, you must add 5 mL of laboratory-grade methanol to a 5 g soil sample.

Advantages of Field Preservation

- The main advantage of field preservation is that the lab does not need to receive the samples within 48 hours.

Limitations on Field Preservation

- The main disadvantage of field preservation is that you must, in the field, do things that are normally done in laboratory. Thus, a lot more things can go wrong; however, field

[8] See Appendix A of Method 5035, Section A.8.2.1.

preservation is certainly not an impossible task, and it can be easily accomplished if you are careful and pay attention to details. For example, you must try to add a precise quantity (~ 5 mL) of preservative and soil (~ 5 g). You must also weigh sample vials prior to and after sample collection.

- You can significantly reduce error by using field kits with pre-preserved and pre-weighed vials; however, these kits can be fairly costly.

- Methanol is a toxic flammable liquid, which presents issues when collecting and shipping samples.

Option 4: Alternative Methods

- Ecology may, on a case-by-case basis, approve of alternative soil VOC sampling methods. This option is designed primarily for future changes in soil VOC sampling technology. *However, Ecology expects that as a matter of policy, all soil VOC samples must be collected in a manner that minimizes volatilization and biodegradation!*

Low- vs. High-Concentration Method: Which One Should I Select?

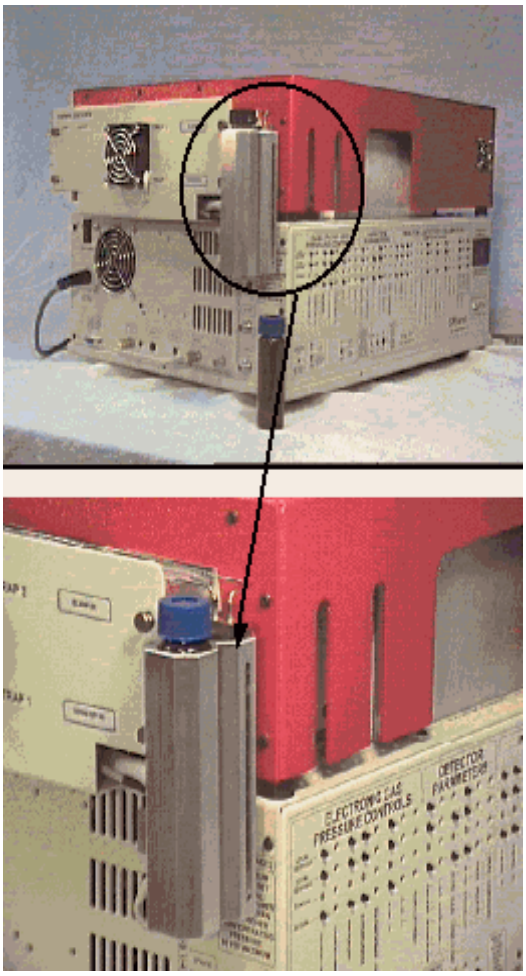
EPA Method 5035A has two main components: a "low-concentration" method and a "high–concentration" method. A brief synopsis of each is as follows:

- The low-concentration method uses sodium bisulfate as a preservative. Detection limits of < 200 ug/kg can be obtained with this method provided soil VOC concentration are < 200 ug/kg.

- The low-concentration method is designed to minimize VOC losses by using the sample container as the "purging" device (hence the name closed-system-purge and trap). Here's how this works: when you collect the sample, it is sealed and sent to the lab. The entire sample vial is then placed, unopened, into the purge and trap "instrument carousel" (Figure 1, p.8). The vial is then heated to 40°C and the volatiles are purged into a "trap".

- The high-concentration method uses methanol as a preservative. The high-concentration method works best for soil VOCs with concentrations > 200 ug/kg. In the high-concentration method, the lab will take a small aliquot (~ 50-100 uL) of the soil-methanol solution and inject it directly into the gas chromatograph (GC). EPA Method 8021B or 8260B is then used for analysis.

Figure 1: EPA Method 5035A "Low-Concentration" Method.



Source: SRI INSTRUMENTS, 20720 Earl Street, Torrance, Calif. 90503 U.S.A.

1. UPPER PHOTO. The 40-mL VOA Vial is inserted into a Gas Chromatograph (GC) with an "Adjustable Temperature Thermostatted Sleeve".

2. LOWER PHOTO. Two needles puncture the septum, one allowing the sparge gas (helium) to enter the vial, the other exhausts the sample into the adsorbent traps.

The advantages and limitations of these two preparation procedures are as follows:

Low-Concentration Method Advantages

- The key advantage of this method is that it allows you to quantify soil VOCs at low concentrations, i.e., < 200 ug/kg. In particular, since you are not adding methanol, there is no dilution factor in the sample extract.

Limitations

- You are not supposed to use this method if soil VOC concentrations are > 200 ug/kg (they will likely exceed the working range of the analytical instrument).

- Because it is a closed-system-purge and trap, the lab can analyze each sample only one time. Thus, it is recommended that you collect 2-3 samples per sample location.

- Calcareous (or sandy) soil will react with the acid solution, which can result in broken or shattered VOA vials.

- Sodium bisulfate is not an efficient extraction medium for VOCs, which impacts recovery rates. This is because VOCs are less likely to dissolve into an acid solution comprised of sodium bisulfate and water.

- Recent studies[9] found that the sodium bisulfate acid solution may oxidize naturally-occurring soil waxes and humic material, which results in increased soil acetone levels.

High-Concentration Method Advantages

- The key advantage of this method is that VOCs will readily dissolve into methanol, which makes it a very efficient extraction medium. Studies[10] on methanol extraction have found that results tended to be more accurate when compared to results from the low-concentration purge and trap method.

- Unlike the low-concentration method, the lab can analyze the sample more than once if necessary.

Limitations

- Prior to analysis, the lab must ***dilute***[11] the sample, which means practical quantitation limits (PQLs)[12] will be ***higher***. For example, if you mix add 5 mL of methanol with 5 g of soil and the lab extracts 100 uL for analysis, the dilution is 50 (5,000 uL/100 uL = 50). With a dilution of 50, you can probably expect to achieve laboratory reporting limits/ PQLs of ~ 25-50 ug/kg.

- Methanol is a highly flammable and toxic liquid, which presents issues for shipping and sample collection. Also, methanol can be easily contaminated by atmospheric sources of VOCs, e.g., car exhaust.

How Do I Know if Soil VOC Concentrations are < or > 200 ug/kg?

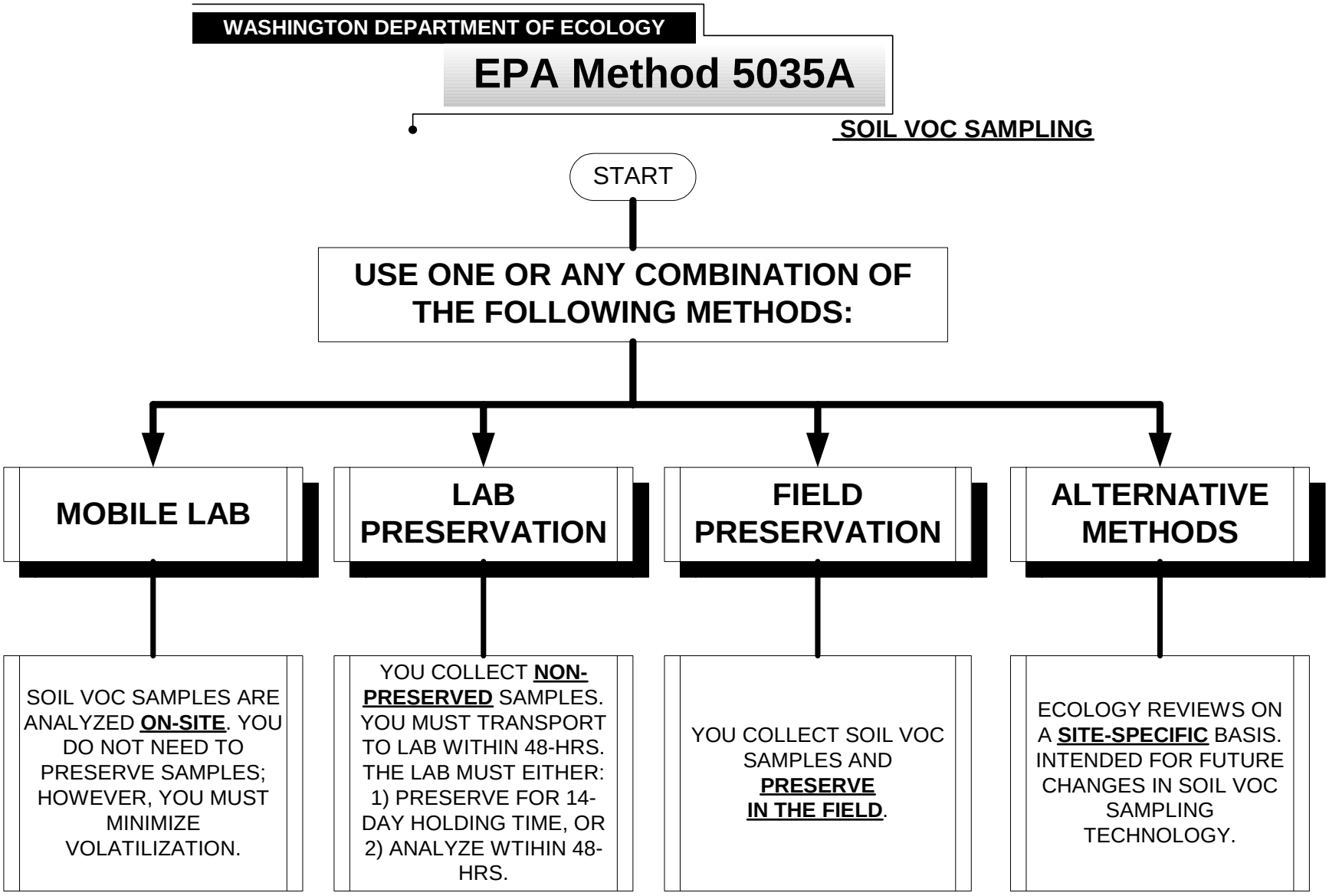
If you opt for the low-concentration method, you will need to check and make sure that soil VOC concentrations are < 200 ug/kg. To do this, you may use field screening instruments[13], or you may instruct the lab to screen samples. Also, before you make any decisions about which method to use, you should always check Ecology's soil cleanup standards. Cleanup levels for nine (9) common VOCs are provided in Table 1.

Table 1: State of Washington Method A Soil VOC Cleanup Levels (Unrestricted Land Use).

Volatile Organic Compound (VOC)	Cleanup Level (ug/kg)
Benzene	30
Ethyl Benzene	6,000
MTBE	100
Naphthalene	10,000
Tetrachloroethylene	50
Toluene	7,000
Trichloroethane-1,1,1	50
Trichloroethylene	30
Xylene	9,000

Source: Table 740-1 (Chapter 173-340 WAC)

[9] See Refs 3, 17, 26.
[10] See Refs 1, 14, 15, 18, 19, 22, 0.
[11] See also EPA 5035A, Section 8.2.2.
[13] See Ref 19.


WASHINGTON DEPARTMENT OF ECOLOGY
EPA Method 5035A
SOIL VOC SAMPLING
START
USE ONE OR ANY COMBINATION OF THE FOLLOWING METHODS:
MOBILE LAB
LAB PRESERVATION
FIELD PRESERVATION
ALTERNATIVE METHODS
SOIL VOC SAMPLES ARE ANALYZED ON-SITE. YOU DO NOT NEED TO PRESERVE SAMPLES; HOWEVER, YOU MUST MINIMIZE VOLATILIZATION.
YOU COLLECT NON-PRESERVED SAMPLES. YOU MUST TRANSPORT TO LAB WITHIN 48-HRS. THE LAB MUST EITHER: 1) PRESERVE FOR 14-DAY HOLDING TIME, OR 2) ANALYZE WTIHIN 48-HRS.
YOU COLLECT SOIL VOC SAMPLES AND PRESERVE IN THE FIELD.
ECOLOGY REVIEWS ON A SITE-SPECIFIC BASIS. INTENDED FOR FUTURE CHANGES IN SOIL VOC SAMPLING TECHNOLOGY.

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Green Bay, WI 54302 (En Novative)

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Appendix A: Soil VOC Sampling Instructions

OVERVIEW

The instructions provided here are **guidelines**. You are, however, legally obligated to follow and meet the criteria specified in WAC 173-340-830. We recognize and understand that sampling protocols vary and that how you do things will vary. Ecology also recognizes that with respect to analytical methods, the "performance based"[14] approach is now gaining widespread acceptance. Ecology compiled these instructions based on a review of other state 5035A policies, the instructions in Method 5035A itself and consultation with others who had historical knowledge of how best to implement Method 5035A.

SOIL VOC SAMPLING INSTRUCTIONS PLEASE NOTE

If you opt for lab preservation, then you may skip STEPS 1-6 and go directly to STEP 7. *The instructions provided in this tech memo are only for the sampling and preservation of soil VOC samples when using methanol or sodium bisulfate as the preservative. The instructions do not include a description of other sampling or preservation procedures, including those involving the freezing of the soil samples. For a complete description of sampling and preservation procedures see EPA Method 5035A.*

[14] EPA defines this is as "a set of processes wherein the data quality needs, mandates or limitations of a program or project are specified, and serve as criteria for selecting appropriate methods to meet those specified needs in a cost effective manner."

WHAT EQUIPMENT WILL I NEED?

Laboratory Preservation

- **Sample containers.** You may use a zero Headspace Extraction (ZHE) container (e.g., **En Core® Sampler)** or other equivalent container.

- **Shipping arrangements.** Products like the En Core® sampler must be shipped to the lab within 48 hours. ***Depending upon the product you use, you must make shipping arrangements ahead of time!***

Field Preservation

- **Vials.** You must use 40-mL "VOA" glass vials with septum sealed Teflon-lined screw caps. All vials must be pre-weighed to the nearest 0.1 g. Record the vial tare weight on the sample label. You can either have the lab do this or you can do it in the field with your field balance.

- **Preservative**. If you are using the **low-concentration method**, then you must use sodium bisulfate ((NaHSO4) preservative. You must mix the preservative (~ 1 g) with at least 5 mL of organic-free reagent water so that the pH of the acid-water solution is ≤ 2. You can either have the lab do this or you can do it in the field. If you are using the **high-concentration method**, then you will need to use laboratory-grade methanol (CH3OH).

- *NOTE: Ecology recommends that you use pre-preserved and pre-weighed vials.*

- **Safety equipment.** Methanol is a toxic and flammable liquid. You will need to wear rubber gloves and other appropriate safety equipment.

- **Soil Sampling Syringes.** Ecology recommends that you use syringes to collect soil samples. Syringes have three distinct advantages: 1) they essentially allow you to collect ***undisturbed samples***, 2) they are calibrated with marks or lines that allow you to pre-determine how much sample is equal to 5 g, and 3) most syringes are designed to prevent ***headspace air*** above the sample contents. You may use several types of commercially available syringes, including: En Novative Technologies Inc. EasyDraw® syringe and Powerstop Handle®, Environmental Sampling Supply (ESS) "Lock N' Load", etc.

- **Balance.** You will need a portable "field" balance that is capable of weighing to 0.1 g. You will also need reference weights so that you can periodically check the balance for accuracy.

SOIL VOC SAMPLING INSTRUCTIONS

- *Note: If you opt for lab preservation, then you may skip STEPS 1-6 and go directly to STEP 7. The following instructions are only for the sampling and preservation of soil VOC samples when using methanol or sodium bisulfate as the preservative. The following instructions do not include a description of other sampling or preservation procedures, including those involving the freezing of the soil samples. For a complete description of sampling and preservation procedures see EPA Method 5035A.*

STEP 1. CHECK LOCATION

- If you are using methanol, then select an area that is free of car exhaust (it will contaminate the methanol).

STEP 2. CHECK SAFETY GEAR

- You should always wear gloves, goggles and other appropriate safety gear.

- *NOTE: methanol (Chemical Abstract Number 67-56-1) is a toxic and flammable liquid. You will need to use proper safety precautions. Ecology recommends that you wear Nitrile Rubber or Viton gloves. Avoid inhalation and make sure you store and use the methanol in a ventilated area, away from ignition sources. In the event of eye contact, flush with large volumes of water and seek medical attention immediately!*

STEP 3. CHECK FIELD BALANCE, AND FIELD-WEIGH 40-mL VOA VIALS

a) Check the calibration of your field balance. Follow manufacturer's instructions and record the check in your field notebook.

b) Reweigh each 40-mL VOA vial that you will be using that day. ***If the difference between the lab tare weight and the field weight is > 0.2 g, then do not use the vial!***

STEP 4. PREPARE METHANOL BLANKS

a) Ecology recommends preparing at least one methanol blank per sample cooler. Here's how this works: while you are collecting your soil VOC samples, you will leave the blank methanol vial open to check for any atmospheric VOCs. When you are done collecting soil samples, you will cap the blank vial and ship it to the lab along with the other samples.

b) **Preparing a methanol blank:** check with the lab about a methanol preservation sampling kit. You will need a tube of methanol and a pre-weighed 40-mL vial. When you are ready in the field, cut off the top of the methanol tube and carefully pour the contents into the 40-mL vial. Affix a label entitled "methanol field blank". Record the identification number in your field notebook. While collecting soil VOC samples, leave the blank methanol vial open. When done collecting soil samples, cap the blank vial and ship it to the lab along with the other samples.

STEP 5. CALIBRATE SOIL SYRINGE

a) If the syringe is already calibrated for 5 g (e.g., EasyDraw Syringe® and Powerstop Handle®; Figure 4, p. 21), then load or insert the syringe into the handle slot that is marked "5 g".

b) If you do not have a pre-calibrated syringe, then do this:

- Weigh an empty syringe on your field balance and record the weight,
- Insert the empty syringe into the soil and collect ~ 5 g soil. Cap the syringe. Make sure you wipe off any excess dirt.
- Reweigh (syringe + soil) and subtract syringe weight to determine soil weight.
- If the soil weight is ~ 5 g, then record how far you had to insert the syringe into the soil to achieve ~ 5 g. Use a trial-and-error method until you determine how far you must insert the syringe.

STEP 6. CHECK FOR CALCAREOUS SOILS

- *NOTE: this step applies only if you are using sodium bisulfate as a preservative. If you are preserving with methanol, then skip this step and go to STEP 7. If you are working in calcareous or carbonate soils, then do not use the sodium bisulfate preservative! The acid solution will react with the soil, which may result in excessive gas buildup and a shattered or broken VOA vial. If you do encounter calcareous soil, then use distilled water as a preservative! If you want to check to see if the soil contains carbonates, then squirt a few drops of hydrochloric acid (HCL) onto the soil. If it fizzes or effervesces, then the soil is calcareous.*

STEP 7. COLLECT SOIL SAMPLES

a) As a general rule of thumb, you should probably **collect at least two samples for every one location you sample**. This is particularly true for the low-concentration (sodium bisulfate) method, as the lab can analyze the sample only one time.

b) If you are using a methanol blank to check for contamination, then open it and place it in a secure area. Cap the vial when you are done collecting samples.

c) If you are using a syringe (e.g., En Core EasyDraw®) to collect samples, you will need to collect an undisturbed soil sample from a freshly exposed surface. To do this, gently push the syringe into the soil to a depth that is ≅ 5 g soil (see Figure 2, p. 20). Remove the syringe from the soil and quickly wipe the barrel end clean. Immediately cap the syringe. Make sure you wipe off any excess dirt.

- *NOTE: the En Core EasyDraw® syringe is not the same device as the En Core® Sampler! The syringe is supposed to be used only to collect and extrude soil into the VOA vial.*

d) If you are using the En Core® Sampler, use the steel T-handle to push the sampler into the soil. Skip Step 8 and go to STEP 10.

e) If the syringe or En Core® Sampler does not penetrate the soil, use a stainless steel spatula or scoop. Try to scoop or remove ~ 5 g soil. Once you've collected your sample, gently fill your 40-mL VOA vial with the appropriate preservative. Go to STEP 8.

STEP 8. EXTRUDE SOIL SAMPLES TO VOA VIALS AND RE-WEIGH.

a) Remove the syringe cap and extrude the 5 g soil sample from the syringe into the 40-mL VOA vial (Figure 3, p. 20). Quickly brush off any soil from the vial threads and **immediately seal the vial with septum and screw-cap!**

- *NOTE: once you've collected the soil sample, you must try to extrude it into the VOA vial with within 10 seconds! Before you screw the cap on, make sure you inspect the VOA vial threads and wipe off any dirt!*

b) **Low-concentration Method.** If you are using the *low-concentration* method (soil VOCs < 200 ug/kg), then you must, for a 5 g soil sample, add ~ 1 g of sodium bisulfate ($NaHSO_4$) to each 40-mL vial. If you are collecting soil samples significantly < or > 5 g, then add ~ 0.2 g of preservative for 1 g of sample, e.g., 25 g sample = 5 g preservative. Add at least 5 mL of organic-free reagent water so that the pH of the acid-water solution is ≤ 2.

c) **High-concentration Method.** If you are using the *high-concentration* method (soil VOCs > 200 ug/kg), then you must add 5 g of soil with 5 mL of laboratory grade methanol (CH_3OH).

d) Gently swirl the vial for ~ 10 seconds to break up the soil particles. DO NOT SHAKE!

e) **Re-weigh** the 40-mL vial. **Your target weight is 5 ± 0.5 g.** Record the sample weight to the nearest 0.1 g in your field notebook. **Do not record the weight on the sample label!**

- *NOTE: **do not** open the vial if you've added too much (or too little) soil. The lab can add more methanol to achieve a 1:1 ratio. The desired ratio of grams soil / mL methanol is 1:1, within a tolerance of +/- 25%. Ratios outside this range may be acceptable, depending upon data quality objectives. In all cases, however, the soil sample must be completely immersed in methanol.*

STEP 9. COLLECT ADDITIONAL SOIL SAMPLES FOR MOISTURE CONTENT ANALYSIS

a) ***For every one location you sample, you must collect at least one soil sample for moisture content analysis!*** The lab must have this information so that it can normalize the soil VOC concentration to a dry-weight basis. You should collect ~ 10 g of soil for moisture content analysis. Do not add preservative to the sample designated for moisture content analysis. Use the EasyDraw® syringe, a 4-oz wide mouth glass jar, a 40-mL VOA vial, or other suitable container for your moisture content analysis. Make sure you label the vial so that the lab knows it's for moisture content analysis!

- *NOTE: Because water is completely miscible with methanol, naturally-occurring soil moisture may result in under-reporting of the true, dry-weight VOC concentrations. As a general rule of thumb, a 1% increase in moisture content (by weight) will result in a negative bias of ~ 1%; however, moisture contents < 25% by weight are generally not considered significant by most labs.*

STEP 10. ICE SAMPLES AND SHIP TO LAB

a) **Once they are sealed and weighed, immediately place all samples on ice @ 4 ± 2° C!**

b) If you are shipping methanol-preserved samples, you must comply with the following requirements:

Methanol Shipping Requirements

- Each 40-mL vial must have < 30 mL of methanol (30 mL falls under the federal exemption for small quantities of flammable liquids).

- The "cooler" or container that you use for shipping must have a total methanol volume of < 500 mL (that's 50 samples @ 10 mL of methanol each).

- You must have sufficient absorbent material in the cooler in case one of the vials breaks. You must have enough to completely absorb the vial's contents.

- The cooler or package weight must not exceed 64 pounds.

- Each cooler or container must be clearly labeled as containing < 500 ml methanol.

- The shipping of methanol is regulated by the U.S. Department of Transportation, Title 49 of the Code of Federal Regulations. The DOT number is UN 1230.

Figure 2: Using a Syringe to Collect the Soil Sample.

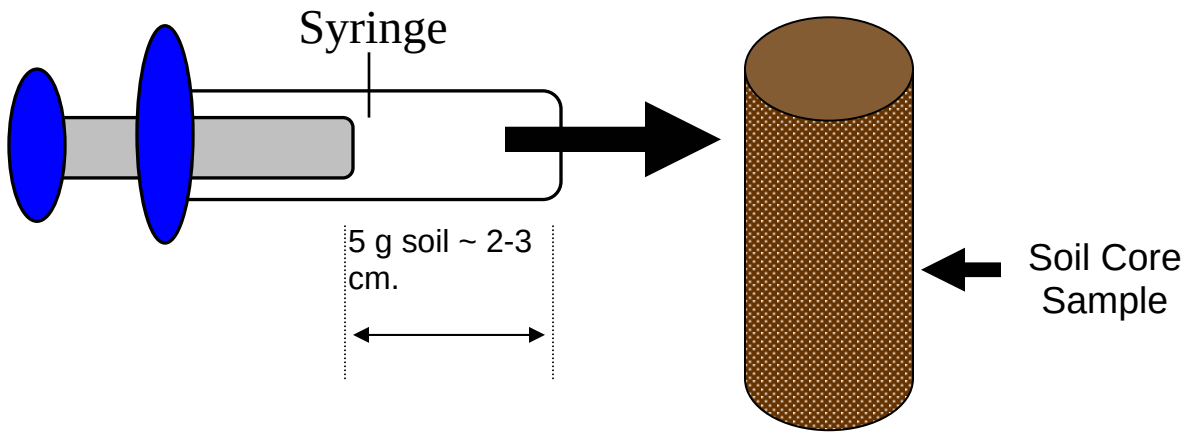

Figure 3: Vial and Sample.

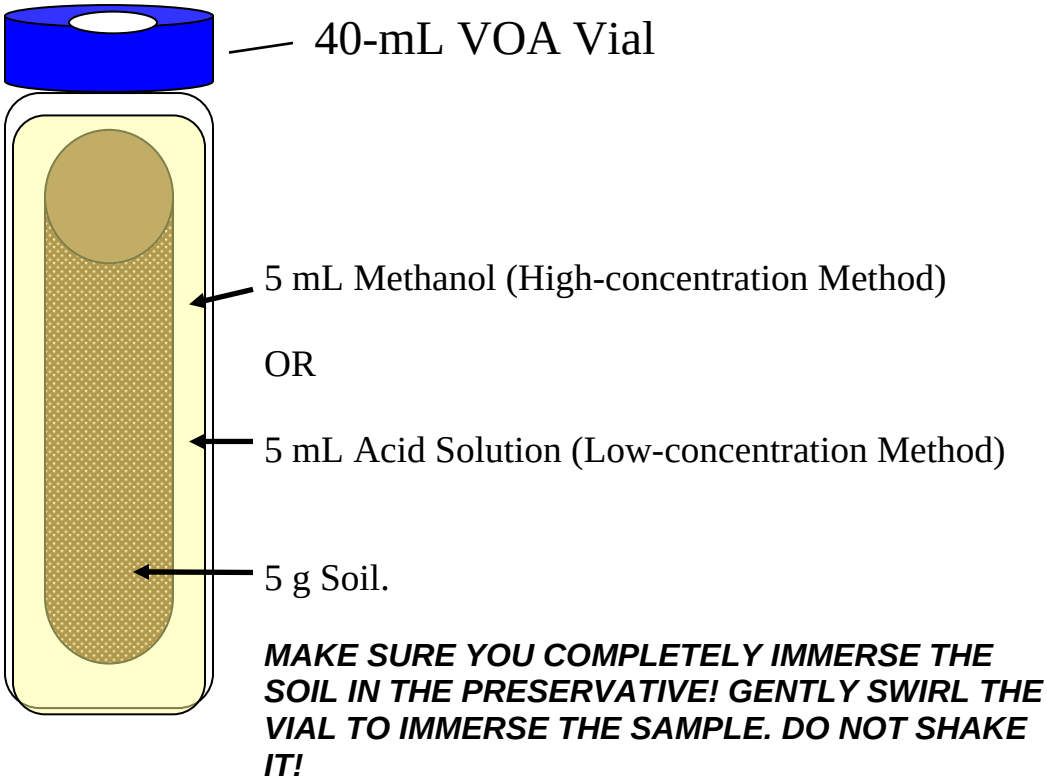

Figure 4: Sample Collection Equipment.

40-mL VOA Vial and Plastic Syringe

"EasyDraw® Syringe & Powerstop Handle®

"En Core®" Soil Core Sampler

En Novative Technologies, Inc.

Terra Core™ Soil Sampler

En Novative Technologies, Inc.

"En Core®" T-Handle

En Novative Technologies, Inc.

Field Balance

Portable Scout* Series Electronic Balance by Ohaus*